DECLARATION

I, Maisy Lim Siaw Chin, a staff member of HIROTA, NAGARE & ASSOCIATES, 4th Floor, Shinjuku TR Bldg., 2-13, Yoyogi 2-chome, Shibuya-ku, Tokyo 151-0053, Japan, do hereby declare that I am well acquainted with the English and Japanese languages and I hereby certify that, to the best of my knowledge and belief, the followings are true and correct translations made by me into the English language of the accompanying copies of the documents in respect of Japanese Patent Application Nos. 2001-134523 filed on May 1, 2001 in the name of Bridgestone Corporation.

Dated this 22nd day of June 2005

Maisy Lim Siaw Chin

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[I. P. C.] G02B 5/22
[INVENTOR]
[ADDRESS OR RESIDENCE] 3-1-1, Ogawahigashi-cho, Kodaira-shi, Tokyo
[NAME] Taichi Kobayashi
[INVENTOR]
[ADDRESS OR RESIDENCE] 3-1-1, Ogawahigashi-cho, Kodaira-shi, Tokyo
[NAME] Masayuki Matsuzaki
[INVENTOR]
[ADDRESS OR RESIDENCE] 3-1-1, Ogawahigashi-cho, Kodaira-shi, Tokyo
[NAME] Masato Sugimachi
[INVENTOR]
[ADDRESS OR RESIDENCE] 3-1-1, Ogawahigashi-cho, Kodaira-shi, Tokyo
[NAME] Yasuhiro Morimura
[APPLICANT]
[I. D. NUMBER] 000005278
[NAME] Bridgestone Corporation
[AGENT]
[I. D. NUMBER] 100107515
[ATTORNEY]
[NAME] Koichi Hirota
[TELEPHONE NUMBER] 03-5304-1471
[ASSIGNEDAGENT]
[I. D. NUMBER] 100107733
[ATTORNEY]
[NAME] Yoshihiro Nagare
[TELEPHONE NUMBER] 03-5304-1471
[ASSIGNEDAGENT]
[I. D. NUMBER] 100114328
[ATTORNEY]
[NAME] Emiko Noto

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[DOCUMENT] Specification 1
[DOCUMENT] Abstract of the Disclosure 1
[PROOF REQUIREMENT] Necessary

[DOCUMENT NAME] Specification
[TITLE OF THE INVENTION] Near-infrared absorption film
[Scope of Claim for a Patent]
[Claim 1]

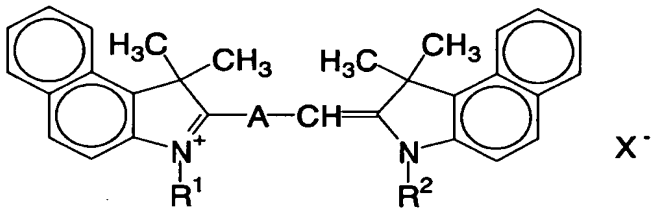
A near-infrared absorption film, comprising:

a transparent substrate; and

a near-infrared absorption layer which comprises a cyanine compound represented by the formula (1), and a diimonium compound,

Formula (1)

[Chemical Formula 1]

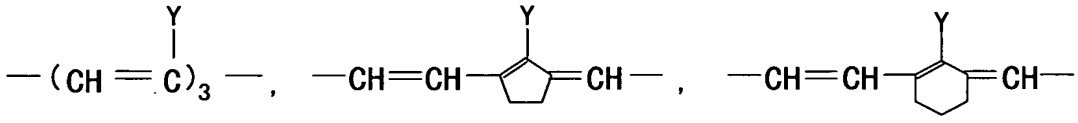


wherein, in the formula (1), "A" is a divalent bonding group comprising an ethylene group. "R^1" and "R^2" are monovalent groups comprising carbon atoms. "X^-" is a monovalent anion.

[Claim 2]

The near-infrared absorption film according to Claim 1, wherein "A" is represented by any one of the formulae (2) to (4):

[Chemical Formula 2]

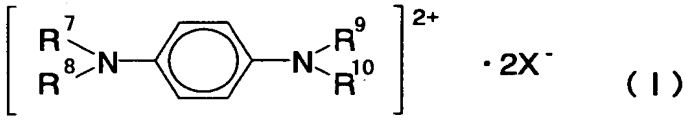


Formula (2) Formula (3) Formula (4)

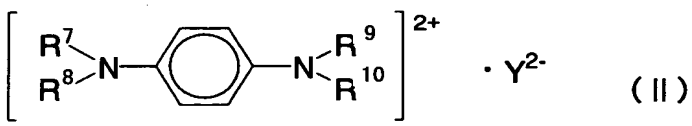
wherein, in formulae (2) to (4), "Y" is any one of an alkyl group, diphenylamino group, halogen atom and hydrogen atom.

[Claim 3]

The near-infrared absorption film according to Claim 1 or Claim 2, wherein the diimonium compound is represented by any one of the formula (I) and (II):
[Chemical Formula 3]



(I)



(II)

wherein, in the formula (I) and (II), "R^7" to "R^{10}" are any one of an alkyl group, an aryl group, a group comprising an aromatic ring, a hydrogen atom and a halogen atom, "X^-" is a monovalent anion, and "Y^{2-}" is a divalent anion.
[Claim 4]
The near-infrared absorption film according to any one of Claim 1 to Claim 3, wherein an amount of the diimonium compound is at least 200 parts by weight relative to 100 parts by weight of the cyanine compound.
[Claim 5]
The near-infrared absorption film according to any one of Claim 1 to Claim 4, wherein the anion represented by "X^-" in formula (1) and the anion represented by "X^-" in formula (I) are identical ions.

[Detailed Description of the Invention]
[0001]
[Technical Field to which the Invention Belongs]
The present invention relates to, particularly, a near-infrared absorption film suitable for disposing on a front surface of a plasma display (PDP).
[0002]

[Prior Art]

In the related art, in general, in electromagnetic wave shield optically transmitting materials disposed on the front surfaces of plasma displays (PDP), a near-infrared ray absorption film which absorbs near-infrared rays that cause malfunctions of other peripheral electronic equipment, is affixed to the PDP side of the display. It is required that this near-infrared absorption film has a high selective near-infrared absorbing ability to effectively block near-infrared rays while having excellent visible light transparency and tone.

[0003]

In order to satisfy the above requirements, various near-infrared absorption films have been studied and proposed in Japanese Patent Application Laid-Open (JP-A) Nos. 09-230134, 10-78509 and 11-316309, but due to technical developments in recent years, infrared absorption films with still higher near-infrared ray blocking power, superior visible light transparency and better appearance have come to be required.

[0004]

[Problems that the Invention is to Solve]

The present invention answers to the needs of the prior art and accomplish the following objects. Namely, the object of the present invention is to provide an infrared absorption film having an excellent near-infrared ray blocking performance and visible light transparency over a wide wavelength range, and an excellent tone.

[0005]

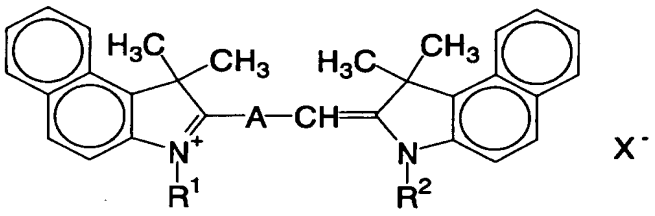
[Means for Solving the Problems]

The means for solving the above-mentioned problems is as followings, namely, <1> a near-infrared absorption film comprises a transparent ("transparence" refers to transparence to "visible light", hereafter idem) substrate, and a near-infrared absorption layer which comprises a cyanine compound represented by the formula (1), and a diimonium compound.

Formula (1)

[0006]

[Chemical Formula 4]



[0007]

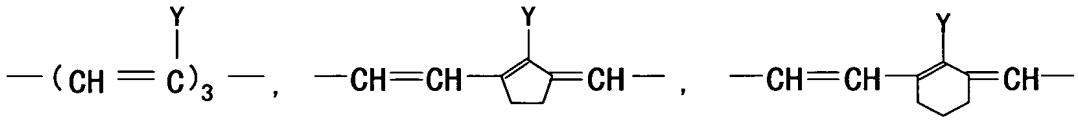
In the formula (1), "A" is a divalent bonding group comprising an ethylene group. "R^1" and "R^2" are monovalent groups comprising carbon atoms. "X^-" is a monovalent anion.

[0008]

<2> The near-infrared absorption film according to the above-mentioned <1>, wherein "A" is represented by at least any one of the formulae (2) to (4):

[0009]

[Chemical Formula 5]



Formula (2) Formula (3) Formula (4)

[0010]

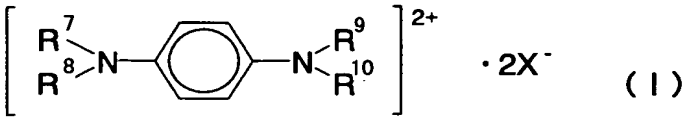
In formulae (2) to (4), "Y" is any one of an alkyl group, diphenylamino group, halogen atom and hydrogen atom.

[0011]

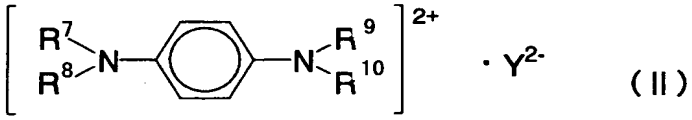
<3> The near-infrared absorption film according to the above-mentioned <1> or <2>, wherein the diimonium compound is represented by at least any one of the formula (I) and (II).

[0012]

[Chemical Formula 6]



(I)



(II)

[0013]

In the formula (I) and (II), "R^7" to "R^{10}" are at least any one of an alkyl group, an aryl group, a group comprising an aromatic ring, a hydrogen atom and a halogen atom. "X^-" is a monovalent anion. "Y^{2-}" is a divalent anion.

[0014]

<4> The near-infrared absorption film according to any one of the above-mentioned <1> to <3>, wherein an amount of the diimonium compound is at least 200 parts by weight relative to 100 parts by weight of the cyanine compound.

<5> The near-infrared absorption film according to any one of the above-mentioned <1> to <4>, wherein the anion represented by "X^-" in formula (1) and the anion represented by "X^-" in formula (I) are identical ions.

[0015]

[Mode for Carrying Out the Invention]

The near-infrared absorption film of the present invention comprises a transparent substrate, and a near-infrared absorption layer, and other layers if required.

[0016]

[Near-infrared absorption layer]

The near-infrared absorption layer comprises a cyanine compound and a diimonium compound, and other components if required.

[0017]

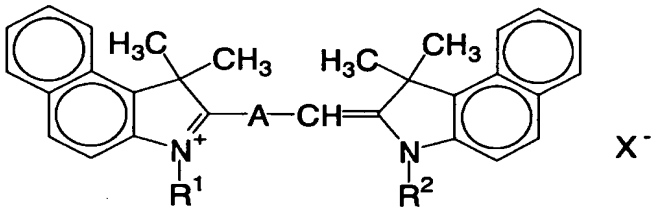
-Cyanine compound-

The cyanine compound is represented by formula (1).

Formula (1)

[0018]

[Chemical Formula 7]



[0019]

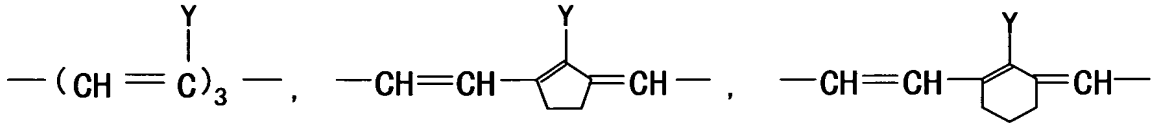
In the formula (1), "A" is a divalent bonding group comprising an ethylene group. "R^1" and "R^2" are monovalent groups comprising carbon atoms. "X^-" is a monovalent anion.

[0020]

It is preferred that "A" in the formula (1) is represented by at least any one of the following formulae (2) to (4) from the viewpoint that they give the film an excellent near-infrared ray blocking performance, excellent visible light transparency and excellent tone.

[0021]

[Chemical Formula 8]



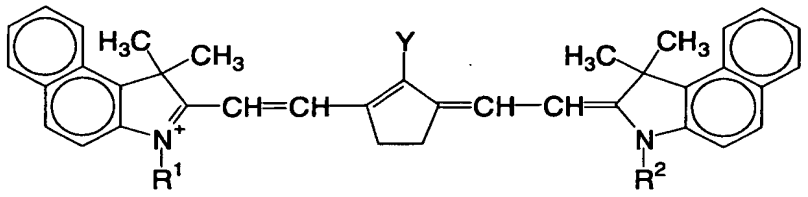
Formula (2) Formula (3) Formula (4)

In formulae (2) to (4), "Y" is any one of an alkyl group, diphenylamino group, halogen atom and hydrogen atom.

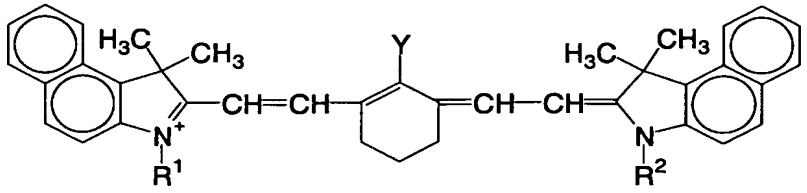
[0022]

In formula (1), a specific example of the case where "A" is formula (3) is shown by formula (5), a specific example of the case where "A" is formula (4) is shown by the formula (6), and a specific example of the case where "A" is formula (2) is shown by formula (7), respectively.

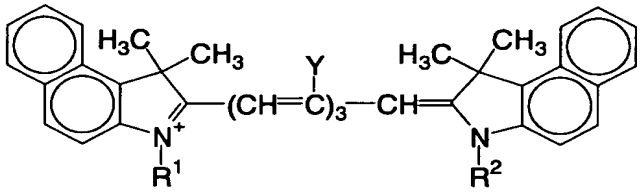
[0023]
[Chemical Formula 9]



Formula (5)



Formula (6)



Formula (7)

[0024]

In formula (1), "R^1" and "R^2" may be an alkyl, an aryl, an alkoxy, an alkoxycarbonyl, a sulfonylalkyl, a cyano, and the like. "X^-" may be I^-, Br^-, ClO_4^-, BF_4^-, PF_6^-, SbF_6^-, $CH_3SO_4^-$, NO_3^-, CH_3-C_6H_4-SO_3^-, and the like.

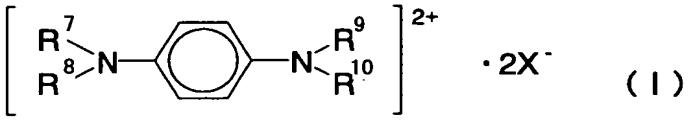
[0025]

-Diimonium compound-

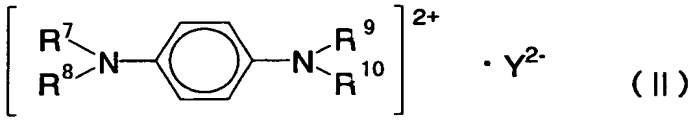
There is no particular limitation on the above-mentioned diimonium compound, but it may be one of the compounds represented by the following formulae (I) and (II)

[0026]

[Chemical Formula 10]



(I)



(II)

[0027]

In the formulae (I) and (II), "R^7" to "R^{10}" are at least any one of an alkyl group, an aryl group, a group comprising an aromatic ring, a hydrogen atom and a halogen atom. "X^-" is a monovalent anion. "Y^{2-}" is a divalent anion.

[0028]

In the formula (I), the monovalent anion represented by "X^-" may be a halogen ion such as I^-, Cl^-, Br^- or F^-, an inorganic acid ion such as NO_3^-, BF_4^-, PF_6^-, ClO_4^-, SbF_6^-, an organic carboxylic acid ion such as CH_3COO^-, CF_3COO^- or benzoic acid ion, an organic sulfonic acid ion such as $CH_3SO_3^-$, $CF_3SO_3^-$, benzenesulfonic acid ion or naphthalene sulfonic acid ion.

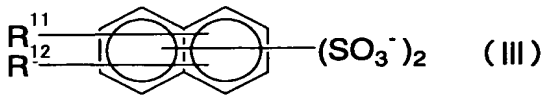
[0029]

In the formula (II), the divalent anion represented by "Y^{2-}" is preferably an aromatic sulfonic acid ion comprising two sulfonic acid groups, for example an ion such as naphthalene-1,5-disulfonic acid, R acid, G acid, H acid, benzoyl H acid (benzoyl bonded to the amino group of H acid), p-chlorobenzoyl H acid, p-toluenesulfonyl H acid, chloro H acid (amino group of H acid replaced by chlorine atom), chloroacetyl H acid, methanyl γ acid, 6-sulfonaphthyl-γ acid, C acid, ε acid, p-toluenesulfonyl R acid, naphthalene disulfonic acid derivatives such as naphthalene-1,6-disulfonic acid and 1-naphthol-4,8-disulfonic acid, carbonyl-J-acid, 4,4-diaminostilbene-2,2'-disulfonic acid, di J acid, naphthalic acid, naphthalene-2,3-dicarboxylic acid, diphenic acid, stilbene-4,4'-dicarboxylic acid, 6-sulfo-2-oxy-3-naphthoic acid, anthraquinone-1,8-disulfonic acid, 1,6-diaminoanthraquinone-2,7-disulfonic acid, 2-(4-sulfophenyl)-6-aminobenzotriazol-5-sulfonic acid,

6-(3-methyl-5-pyrazolonyl)-naphthalene-1,3-disulfonic acid, 1-naphthol-6-(4-amino-3 sulfo) anilino-3-sulfonic acid, and the like. Among these, naphthalene disulfonic acid ion is preferred, the ion represented by the formula (III) being particularly preferred.

[0030]

[Chemical Formula 11]



(III)

[0031]

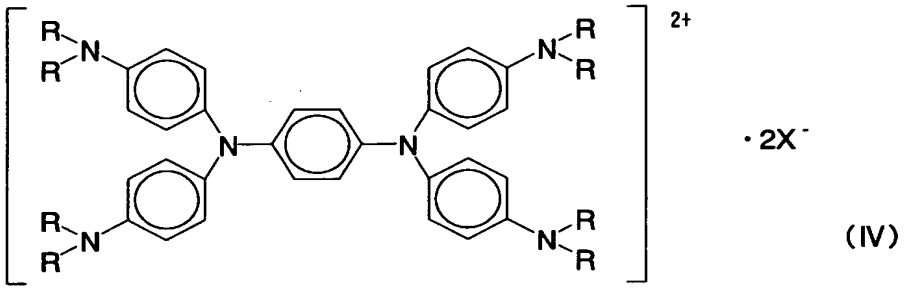
In the formula (III), "R^{11}" and "R^{12}" are at least any one of a lower alkyl group, hydroxyl group, alkylamino group, amino group, -NHCOR^{13}, -NHSO$_2$R^{13} and -OSO$_2$R^{13} (wherein "R^{13}" represents at least any one of an aryl and alkyl group, and "R^{13}" may comprise a substituent), acetyl group, hydrogen atom and halogen atom.

[0032]

The above-mentioned diimonium compound may be preferably the compound represented by the formula (IV).

[0033]

[Chemical Formula 12]

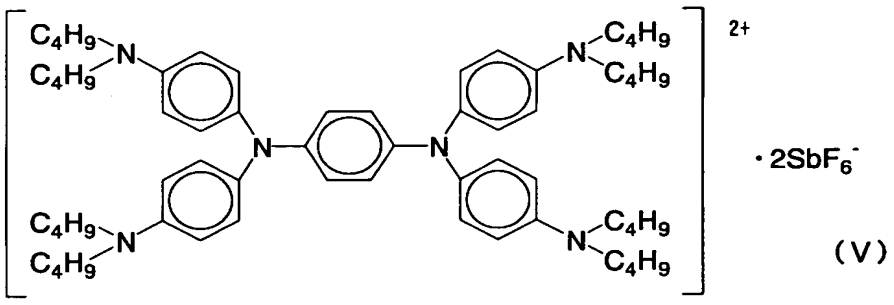


(IV)

[0034]

In the formula (IV), "R" is an alkyl group having 1 to 8 carbon atoms, n-butyl being particularly preferred. "X$^-$" may be preferably BF_4^-, PF_6^-, ClO_4^- or SbF_6^-. A preferred example of this diimonium compound is shown by the formula (V).

[0035]
[Chemical Formula 13]



(V)

[0036]

The anion represented by "X^-" in the formula (1) and the anion represented by "X^-" in the formula (I) are preferably identical, i.e., the counter anions in the above-mentioned cyanine compound and diimonium compound, are preferably identical. If these ions are identical, a near-infrared absorption layer having excellent heat-resisting property and oxidation resistance is obtained.

[0037]

The amount of the above-mentioned diimonium compound is preferably at least 200 parts by weight, and more preferably 200 parts by weight to 2,000 parts by weight, relative to 100 parts by weight of the above-mentioned cyanine compound.

If the amount is more than 200 parts by weight, the diimonium compound not only has an excellent near-infrared absorption effect, but also has an excellent antioxidant effect on the above-mentioned cyanine compound.

[0038]

-Other components-

Examples of other components are various binder resins, near-infrared absorbents other than the above-mentioned diimonium compound (e.g., near-infrared absorbents such as those of the phthalocyanine, nickel complex, azo, polymethine, diphenylmethane, triphenylmethane and quinone types), antioxidants (e.g., antioxidants such as those of the phenol, amine, hindered phenol, hindered amine, sulfur, phosphoric acid, phosphorous acid and metal complex types), ultraviolet absorbers, colorants for making the film more attractive,

pigments, dyes, and the like.

[0039]

The binder resin may be a homopolymer or a copolymer of polyester resin, acrylic resin, methacrylic resin, urethane resin, silicone resin, phenol resin, (meth)acrylic acid ester, and the like. Among these, acrylic resin and polyester resin are preferred from the viewpoint that the diimonium compound and cyanine compound have excellent dispersibility therein, and high durability is obtained.

[0040]

It is preferred that the amount of cyanine compound is 0.1 parts by weight to 10 parts by weight and the amount of diimonium compound is 0.1 parts by weight to 20 parts by weight, and more preferred that the amount of cyanine compound is 0.1 parts by weight to 5 parts by weight and the amount of diimonium compound is 0.1 parts by weight to 10 parts by weight, relative to 100 parts by weight of the binder resin.

[0041]

There is no particular limitation on the thickness of the near-infrared absorption layer described above, but from the viewpoint of near-infrared absorptivity and visible light transparency, it is preferably of the order of 0.5μm to 50μm.

[0042]

[Transparent substrate]

There is no particular limitation on the material of the transparent substrate, which may for example be a resin of polyolefine, e.g., polyethylene or polypropylene, a resin of polyester, acrylic, cellulose, polyvinyl chloride, polycarbonate, phenolic or urethane, and the like. Among these, polyester resin is particularly preferred in respect of transparency and environmental robustness.

[0043]

There is no particular limitation on the thickness of the transparent substrate, but from the viewpoints of mechanical strength and thinness, it is preferably of the order of 50μm to 200μm.

[0044]

[Manufacture of near-infrared absorption film]

There is no particular limitation on the method of manufacturing the near-infrared absorption film, for example, the above-mentioned cyanine compound, diimonium compound and binder resin are

dissolved in a predetermined solvent to prepare a coating solution which is then coated on the transparent substrate surface. The predetermined solvent may for example be dichloromethane, methyl ethyl ketone, tetrahydrofuran, cyclohexanone, and the like.

[0045]

[Composition of near-infrared absorption film]

There is no particular limitation on the composition of the near-infrared absorption film, but it is preferred that the near-infrared absorption layer is a single layer as this makes it very easy to manufacture, and permits it to be made thinner.

[0046]

[Examples]

The present invention will now be described by means of specific examples, but it should be understood that the present invention is not be construed as being limited in any way thereby.

[0047]

(Examples 1 to 7, Comparative Examples 1 to 7)

-Manufacture of near-infrared absorption film-

The amounts of the near-infrared absorption agents and binder resins respectively shown in the "near-infrared absorption agents" and "binder resins" of Tables 1 to 2, were dissolved in a mixed solution of 18.5g dichloromethane, 55.5g tetrahydrofuran and 18.5g cyclohexanone to prepare a coating solution. The coating solution obtained was coated by a bar coater on the surface of a polyester film (transparent substrate, T600E/W07 grade, Mitsubishi Polyester Film Corporation) of width 200mm and thickness 100μm, and dried at 100 °C for 3 minutes to form a near-infrared absorption layer (5μm). In this way, a near-infrared absorption film was manufactured.

This infrared absorption film was evaluated together with a film adjusted by red dye (BRDOU) and blue dye (Sumitomo Chemical Company Limited manufactured BLUE-S) so that the chromaticity (X, Y) was (0.310, 0.316).

[0048]
[Table 1]

Example	Near infrared adsorption agent			Binder resin		
	Compound	Product name	g	Compound	Product name	g
Ex. 1	Diimonium compound	CIR1081	0.48	Polyester resin	UE3690	7.5
	Cyanine compound	NK5578	0.063			
Ex. 2	Diimonium compound	IRG022	0.48	Polyester resin	UE3690	7.5
	Cyanine compound	NK5578	0.063			
Ex. 3	Diimonium compound	CIR1081	0.48	Polyester resin	UE3690	7.5
	Cyanine compound	NK5706	0.075			
Ex. 4	Diimonium compound	IRG022	0.48	Polyester resin	UE3690	7.5
	Cyanine compound	NK5706	0.075			
Ex. 5	Diimonium compound	NIR-IM2	0.48	Polyester resin	UE3690	7.5
	Cyanine compound	NK5706	0.075			
Ex. 6	Diimonium compound	CIR1081	0.48	Polymethyl methacrylate	80N	7.5
	Cyanine compound	NK5706	0.066			
Ex. 7	Diimonium compound	IRG022	0.48	Polymethyl methacrylate	80N	7.5
	Cyanine compound	NK5706	0.063			

[0049]
[Table 2]

Comparative Example	Near infrared absorption agent			Binder resin		
	Compound	Product name	g	Compound	Product name	g
Comp. Ex. 1	Diimonium compound	CIR1081	0.48	Polyester resin	UE3690	7.5
	Phthalocyanine compound	EX811K	0.45			
Comp. Ex. 2	Diimonium compound	CIR1081	0.48	Polyester resin	UE3690	7.5
	Metal complex	MIR101	0.36			
Comp. Ex. 3	Diimonium compound	CIR1081	0.48	Polymethylmethacrylate	80N	7.5
	Metal complex	MIR101	0.38			
Comp. Ex. 4	Diimonium compound	CIR1081	0.48	Polymethylmethacrylate	80N	7.5
	Metal complex	SIR128	0.38			
Comp. Ex. 5	Cyanine compound	NK5706	0.075	Polyester resin	UE3690	7.5
Comp. Ex. 6	Diimonium compound	CIR1081	0.48	Polyester resin	UE3690	7.5
Comp. Ex. 7	Diimonium compound	CIR1081	1.2	Polyester resin	UE3690	7.5

[0050]

In Tables 1 and 2, [NK5578] and [NK5706] are manufactured by Hayashibara Biochemical laboratories (wherein "X-" is SbF_6^-), [CIR1080] is manufactured by Japan Carlit Co., Ltd. (wherein "X-" is SbF_6^-). [IRG022] is manufactured by Nippon Kayaku Co., Ltd. (wherein "X-" is SbF_6^-), [NIR-IM2] is manufactured by Teikoku Chemical Industries (wherein "X-" is SbF_6^-), [EX811K] is manufactured by Nippon Shokubai Co., Ltd., [MIR101] is manufactured by Midori Kagaku Co., Ltd., [SIR128] is manufactured by Mitsui Toatsu Chemicals, [UE3690] is a polyester resin [Elitel UE3690] manufactured by Unitika Ltd., and [80N] is a polymethylmethacrylate resin [Delpet 80N] manufactured by Asahikasei Corporation.

[0051]

<Evaluation>

-Measurement of near-infrared transmittance and luminous transmittance-

On the obtained near-infrared absorption films, the near-infrared transmittance thereof, and the luminous transmittance thereof under a light source C (JIS Z 8701) were measured using a spectrophotometer (U-4000, manufactured by Hitachi Measuring Instruments).

If the luminous transmittance was 70% or more, the film was rated ○, and if it was less than 70%, it was rated ×. For near-infrared transmittance, if the transmittances in the wavelength region of 800nm to 1,100nm were all less than 20%, the film was rated ○, and if the transmittance was 20% or more, the film was rated ×. Tables 3 and 4 show the results.

[0052]

-Durability Test-

The near-infrared absorption films obtained were subjected to two durability tests, i.e., leaving the film at 80°C for 500 hours, and leaving the film under a carbon arc using a sunshine weather meter (Suga tester) at an irradiation intensity of 100 W/m^2 for 24 hours. Subsequently, the durability (heat resistance and antioxidation properties) was evaluated according to the following evaluation criteria. Tables 3 and 4 show the results.

[0053]

--Durability test criteria--

· very excellent durability ···◎

· excellent durability, no problem in practice ···○

· inferior durability ···×

[0054]
[Table 3]

Example No.		Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7
Near infrared transmittance (%)	800nm	19.7	19.7	19.5	19.5	19.5	19.1	19.1
	850nm	4.6	4.6	2.7	2.7	2.7	3.5	3.5
	900nm	9.5	9.5	6.5	6.5	6.5	6.7	6.7
	950nm	4.3	4.3	4.3	4.3	4.3	4.7	4.7
	1000nm	3.4	3.4	3.5	3.5	3.5	4.2	4.2
	1100nm	2.1	2.1	2.1	2.1	2.1	2.4	2.4
	MAX	19.7	19.7	19.5	19.5	19.5	19.1	19.1
Luminous transmittance (%)		74.2	74.2	71.6	71.6	71.6	73.4	73.4
Chromaticity	x	0.310	0.310	0.310	0.310	0.310	0.310	0.310
	y	0.316	0.316	0.316	0.316	0.316	0.316	0.316
Visible light transmittance rating		○	○	○	○	○	○	○
Near infrared transmittance (%) rating		○	○	○	○	○	○	○
Durability rating		◎	◎	◎	◎	◎	◎	◎

[0055]
[Table 4]

Comparative Example No.		Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6	Comp. Ex. 7
Near infrared transmittance (%)	800nm	19.8	19.7	19.6	19.9	35.9	49.1	19.6
	850nm	4.0	5.3	6.4	6.4	8.2	29.3	5.4
	900nm	3.0	2.6	3.5	3.4	50.8	11.6	0.5
	950nm	3.5	2.1	3.1	3.1	87.7	4.4	0.1
	1000nm	3.2	2.8	3.6	3.7	91.4	3.4	0.0
	1100nm	2.1	2.1	2.4	2.4	91.2	2.1	0.0
	MAX	19.8	19.7	19.6	19.9	91.6	49.1	19.6
Luminous transmittance (%)		61.7	63.9	68.1	68.5	84.1	76.5	60.3
Chromaticity	x	0.310	0.310	0.310	0.310	0.310	0.310	0.310
	y	0.316	0.316	0.316	0.316	0.316	0.316	0.316
Visible light transmittance rating		×	×	×	×	○	○	×
Near infrared transmittance (%) rating		○	○	○	○	×	×	○
Durability rating		○	○	○	○	×	○	○

[0056]

From Tables 3 and 4, it is seen that, in Examples 1 to 7 as compared to Comparative Examples 1 to 7, near-infrared blocking properties and visible light transparency are both excellent.

[0057]

[EFFECTS OF THE INVENTION]]

According to the present invention, a near-infrared absorption film having excellent near-infrared blocking properties and visible light transparency over a wide wavelength range, and attractive appearance can be provided.

[DOCUMENT NAME] Abstract of Disclosure

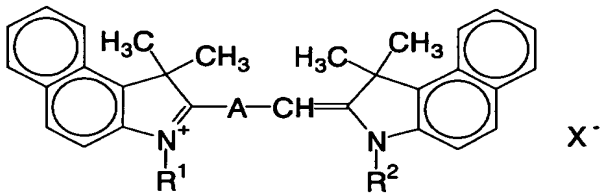
[ABSTRACT]

[PROBLEM TO BE SOLVED] The present invention provides a near-infrared absorption film having excellent near-infrared blocking properties and visible light transparency over a wide wavelength range, and attractive appearance.

[SOLVING MEANS] A near-infrared absorption film comprises a transparent substrate and a near-infrared absorption layer which comprises a cyanine compound represented by formula (1), and a diimonium compound. It is preferable that "A" is an embodiment represented by at least any one of formulae (2) to (4), and an amount of the diimonium compound is an embodiment of at least 200 parts by weight relative to 100 parts by weight of the cyanine compound.

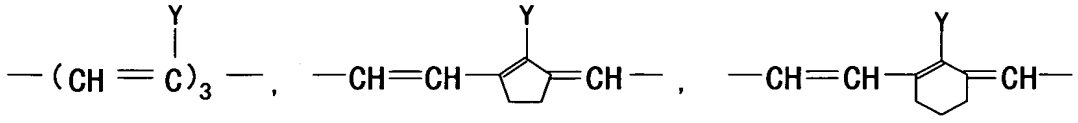
Formula (1)

[Chemical Formula 1]



In formula (1), "A" is a divalent bonding group comprising an ethylene group. "R^1" and "R^2" are monovalent groups comprising carbon atoms. "X^-" is a monovalent anion.

[Chemical Formula 2]



Formula (2) Formula (3) Formula (4)

In formulae (2) to (4), "Y" is any one of an alkyl group, diphenylamino group, halogen atom and hydrogen atom.

[SELECTED DRAWINGS] None